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METHOD FOR PREPARATION OF SELF-IMMOBILIZING POST-METALLOCENE NICKEL OLEFIN POLYMERIZATION CATALYST

Inventors:	Jin Guoxin, Zhang Dao
Applicant:	Changchun Institute of Applied Chemistry, Chinese Academy of Sciences No. 159, Ren Min Street, Changchun, Jilin 130022
Patent Agency:	Changchun Keyu Patent Agency Limited Liability Company
Agent:	Cao Guizhen

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Abstract

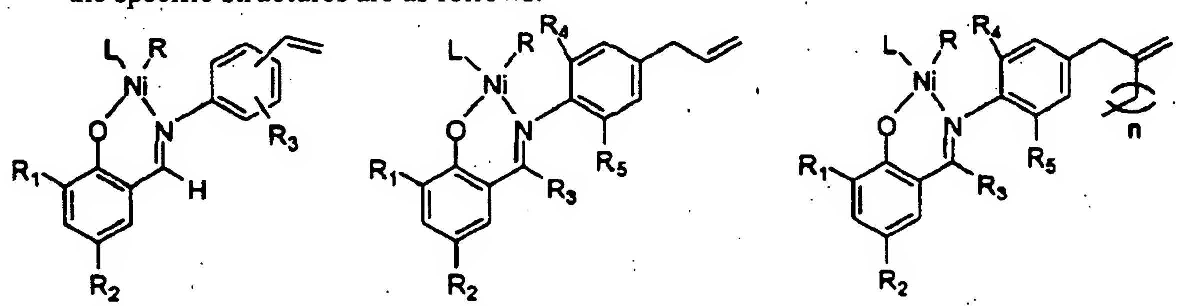
The present invention pertains to a method for preparation of self-immobilizing transition metal post-metallocene nickel olefin polymerization catalyst. The catalyst comprises a single component A or two components A and B with component A expressed as [Comp(M-ANO)], in which Comp is a coordination compound, M is a post-transition metal nickel catalyst and ANO

is an olefin-substituted o-hydroxylimide nitrogen and oxygen bidentate ligand. Component B is cyclooctadiene nickel [$Ni(COD)_2$] or pentafluorophenyl borane [$B(C_6F_5)_3$]. The present type of catalyst has a relatively high catalytic activity with regard to ethylene polymerization, and most importantly, the present type of catalyst does not require any auxiliary catalyst.

Claims

1. A method for preparation of self-immobilizing post-metallocene nickel olefin polymerization catalyst, characterized by the fact that the prepared catalyst comprises a single component A or two components A and B with component A expressed as [Comp(M-ANO)], in which Comp is a coordination compound, M is a post-transition metal nickel catalyst and ANO is an olefin-substituted salicylaldehyde [sic] imide nitrogen and oxygen bidentate ligand;

the specific structures are as follows:

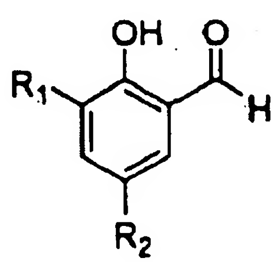


in which R_1 and R_2 are any one of H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen, Anth, Trityl, TPhen, OMe, and NO_2; R_3, R_4 and R_5 are any one of H, Me, ^{i}Pr, and ^{t}Bu; R = Ph, L = PPh_3; n = 0, 1, 2, 3 or 4; component B is any one of cyclooctadiene nickel [$Ni(COD)_2$] or pentafluorophenyl borane [$B(C_6F_5)_3$];

the process for the preparation of the catalyst is as follows:

1) a. Preparation of substituted salicylaldehyde

The structure of the above is:



In an inert gas atmosphere, 0.05-0.1 mol substituted phenol, 0.005-0.01 mol tin tetrachloride catalyst and 0.02-0.04 mol organic amine, specifically triethylamine, tributylamine or piridine, are added to a reactor containing 100-200 mL toluene; after stirring for 20-30 min,

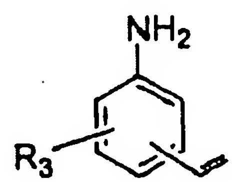
3.3-6.6 g of a polyaldehyde are added, heating is carried out at 100 ± 0.5°C for reflux for 8-12 h; the reaction mixture is acidified by 10% hydrochloric acid to pH = 1-2, extraction with ethyl ether is carried out 3-5 times, followed by washing with 30 mL saturated aqueous table salt solution and then it is dried for 12 h over anhydrous sodium sulfate; rotary evaporation is then carried out to remove the solvent and a crude product is obtained; the crude product is separated and purified by steam distillation, recrystallization or silica gel chromatography to obtain an oily liquid or a solid powder with a yield of 51-87%,

b. Preparation of substituted salicylaldehyde

0.09 mol salicylaldehyde is dissolved in 0.45 mol acetic acid, the temperature of the ice water bath is maintained below 5°C; 0.135 mol fuming sulfuric acid is added dropwise over 8 h; this is stirred overnight, the temperature is then increased slowly to 45°C; after the reaction is carried out for 5 h, cooling and filtration are carried out and the filtrate is washed three times with ice water to obtain 10.6 g of a light-yellow mixture of 3-nitro-2-hydroxybenzaldehyde and 5-nitro-2-hydroxybenzaldehyde with a yield of 95%; 6.6 g of the above mixture are added slowly to a mixed solution of 3.86 mL concentrated sulfuric acid that has been cooled in an ice and calcium chloride bath and 7.72 mL fuming sulfuric acid, reaction is carried out for 30 min until the light-yellow powder is completely dissolved, and a reddish brown viscous reaction product is obtained, which is poured onto a block of ice to precipitate a large amount of lemon-yellow solids, then filtration is carried out followed by recrystallization from benzene to obtain 7.7 g of pure product 3,5-dinitro-2-hydroxybenzaldehyde with a yield of 86%;

2) Preparation of ethylene-substituted aromatic amine

The structure of the above is:

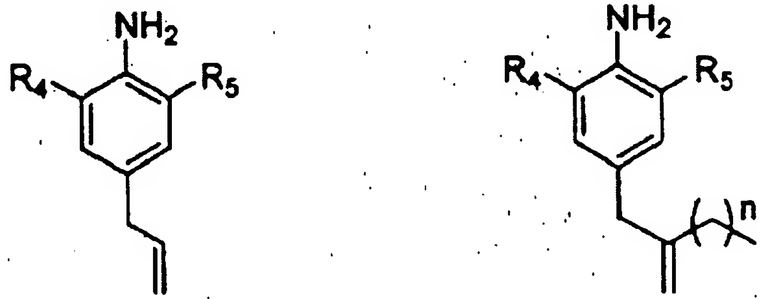


In the absence of oxygen and water, 51-74 mmol methyltriphenylphosphorus bromide and 51-78 mmol n-butyllithium are added to 50-70 mL of dry tetrahydrofuran, cooled with ice water, as the solvent, to carry out a reaction for 30-60 min. 50-74 mmol of a nitro aromatic aldehyde are then added to carry out a reaction for 12-18 h, the resulting mixture is washed with an aqueous salt solution, extracted with chloroform, dried over anhydrous sodium sulfate and then concentrated under vacuum; the remaining solution is purified by silica gel chromatography, the eluent is toluene:ethane [sic; possibly, ethanol] 1:1, a nitro aromatic

ethylene is obtained with a yield of 72-89%, a reduction reaction is then carried out using the ion [sic; iron] – acetic acid – ethyl alcohol system to obtain an olefin aromatic amine with a yield of 56-60%,

3) Preparation of allyl aromatic amine

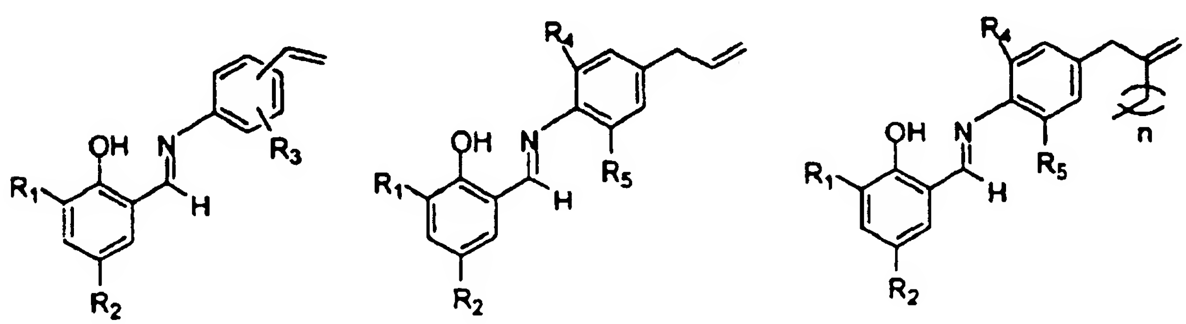
The structure of the above is:



0.1-0.2 mol aromatic amine and 0.05-0.1 mol alkenyl chloride or alkenyl bromide are heated to carry out a reflux reaction for 8-10 h, left standing to cool overnight, and then poured into 200-400 mL water, the solution is alkalized with a sodium hydroxide solution, extracted with chloroform, the pressure is reduced to a vacuum followed by distillation to obtain a N-olefin aniline with a yield of 30-84%; 0.05-0.2 mol N-olefin aromatic amine and 0.05-0.2 mol anhydrous zinc chloride are added to 50-200 mL toluene as the solvent, and reflux is carried out in an argon atmosphere for 5-8 h. After cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution, dried over anhydrous magnesium sulfate, the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain a 4-allyl aromatic amine with a yield of 25-71%,

4) Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

The structure of the above is:



In an inert gas atmosphere, using 10-30 mL methyl alcohol or ethyl alcohol as the solvent and 1 drop of 2 mL formic acid as the catalyst, a reaction is carried out between 2 mmol substituted salicylaldehyde and 2.1 mol olefin aromatic amine is carried out at room temperature for 8-72 h, the mixture from the reaction is cooled, filtered, washed with cold methyl alcohol or ethyl alcohol, and dried under vacuum to obtain a yellow o-hydroxylimide nitrogen and oxygen bidentate ligand with a yield of 70-90%;

5) Preparation of catalyst component A

In the absence of oxygen and water, 1.5 mmol o-hydroxylimide nitrogen and oxygen bidentate ligand are dissolved in 50 mL tetrahydrofuran, the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 4-8 h; filtration is then carried out and the solvent is removed under vacuum to obtain a ligand sodium salt; the above sodium salt is then dissolved in a benzene solution, gradually added dropwise to a benzene solution in which 1.44 mmol trans-$[Ni(Ph)Cl(PPh_3)_2]$ are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent, washing twice with n-ethane, and drying under vacuum to obtain a powdery catalyst solid with a yield of 74-87%;

6) Ethylene polymerization

In the absence of oxygen and water, using 120 mL toluene or n-ethane as a solvent, 10-65 μmol catalyst and, optionally, an auxiliary catalyst, $[Ni(COD)_2]$ or $[B(C_6H_5)3]$ [sic; $[B(C_6F_5)_3]$] of twice the amount, are added to a 500-mL glass reactor; after the gas is purged three times, a polymerization reaction is carried out at room temperature and 2-7 atm of ethylene pressure for 50 min to 1.5 h while stirring; a methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain the product. The catalyst activity is 10^5 g PE/(mol•Ni•h) [sic; (mol Ni•h)].

2. A method for preparation of self-immobilizing post-metallocene nickel olefin polymerization catalyst in accordance with Claim 1, characterized by the fact that in the above catalyst system, R_1 and R_2 are H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen, or NO_2.

Description

The present invention pertains to a method for preparation of self-immobilizing post-metallocene nickel olefin polymerization catalyst.

As one of the most important polymer materials, the availability of polyolefins has greatly improved the living conditions and environment for human beings. Olefins form polymers under the effect of a catalyst, and by changing the structure of the catalyst, it is

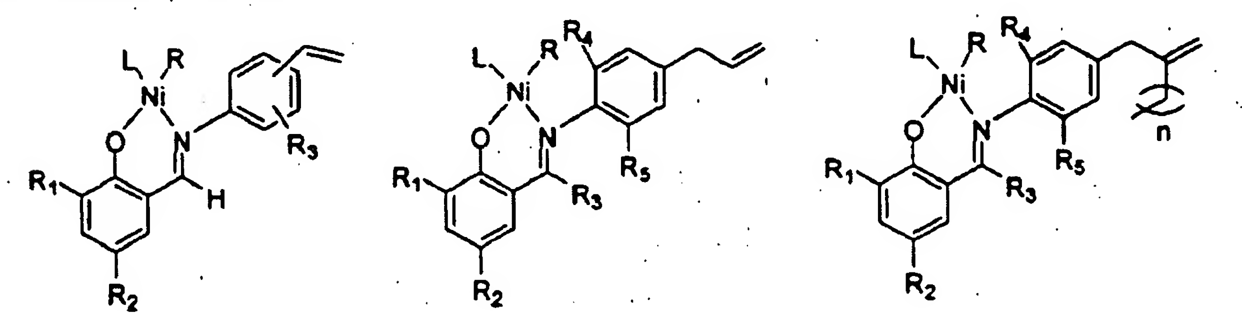
possible to obtain a polyolefin product with a specific molecular structure and specific properties. For this reason, the catalyst has become the core of the original drive toward constant improvement and advancement in upgrading polyolefins. Starting from the end of the last century, post-metallocene post-transition metal catalysts have become the new generation olefin polymerization catalysts with high activity following in the steps of Ziegler-Natta catalysts and metallocene catalysts. They have become the focus of studies on new types of olefin polymerization catalysts all over the world. A post-transition metal catalyst is an organometallic compound of post-transition metals such as nickel, palladium, iron, cobalt and the like. This type of catalyst not only has high activity, is inexpensive and easily obtainable, and is capable of serving in ethylene or α-olefin polymerization as a catalyst to obtain polymers of high molecular weight, but it can also be used as a catalyst in the copolymerization of polar monomers and olefin, which is a characteristic not displayed by the previous two generations of catalysts. A large amount of funding has been invested in its research and development in many countries in Europe and the U.S., for example by companies like DuPont and B. P. Chemistry.

Not long ago, the Grubbs study group from the U.S. (Science, 2000, 287, 460-462; Organometallics, 1998, 17, 3149-3151) reported a new type of neutral nickel olefin polymerization catalyst of a single component which not only displayed a high activity but also could produce polyethylene of high molecular weight. It also exhibited an extraordinarily strong tolerance of impurity atoms such as oxygen, nitrogen and sulfur, and could carry out copolymerization with polar monomers. The most remarkable fact is that this type of post-transition metal olefin polymerization catalyst does not require an auxiliary catalyst such as MAO, $Ni(COD)_2$ or the like. As a result, the requirement for monomer purity of the starting raw material is greatly reduced, which is more convenient for production on an industrial level. At the same time, this pioneering work conveniently opens the door for the polymerization of olefins containing a polar functional group and for the production of polymers with special properties such as biodegradability, surface modification and the like. The self-immobilization function of this type of catalyst has not yet been reported. In order to realize the controllable polymerization of this type of catalyst, to improve the catalytic activity, to obtain polymers of ideal molecular weight and degrees of branching and to adapt to production equipment on an industrial scale, the self-immobilization function is significant.

The objective of the present invention is to provide a method for the preparation of a self-immobilizing post-metallocene olefin polymerization catalyst. The above method uses aromatic amines containing an olefin substitute group to react with substituted salicylaldehyde to form an organic nitrogen and oxygen bidentate ligand. This is followed by a reaction with the alkyl compound of nickel to form a self-immobilizing post-metallocene post-transition metal olefin polymerization catalyst containing an olefin group.

When the self-immobilizing post-metallocene post-transition metal olefin polymerization catalyst is used in the olefin polymerization process, copolymerization occurs between the olefin and the olefin radical on the catalyst to the effect that the catalyst is immobilized on the polyolefin bond and, in this way, the catalytic effect of the active site can be utilized to the maximum degree. Polymerization tests indicate that the catalyst has a relatively high activity with regard to olefin polymerization that can be as high as several times to scores of times that of self-immobilizing catalysts of similar types.

The catalyst prepared in accordance with the present invention comprises a single component A or two components A and B, with component A expressed as [Comp(M-ANO)], in which Comp is a coordination compound, M is a post-transition metal nickel catalyst and ANO is an olefin-substituted salicylaldehyde imide nitrogen and oxygen bidentate ligand. The specific structures are as follows:

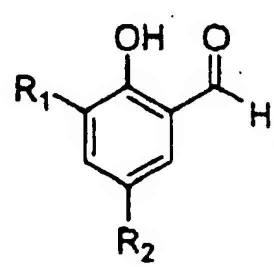


in which R_1 and R_2 are any one of H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen, Anth, Trityl, TPhen, OMe, and NO_2; R_3, R_4 and R_5 are any one of H, Me, ^{i}Pr, and ^{t}Bu; R = Ph, L = PPh_3; n = 0, 1, 2, 3 or 4; component B is any one of cyclooctadiene nickel [$Ni(COD)_2$] or pentafluorophenyl borane [$B(C_6F_5)_3$].

The process for the preparation of the catalyst is as follows:

1) a. Preparation of substituted salicylaldehyde

The structure of the above is:



In an inert gas atmosphere, 0.05-0.1 mol substituted phenol, 0.005-0.01 mol tin tetrachloride catalyst and 0.02-0.04 mol organic amine, specifically triethylamine, tributylamine or piridine, are added to a reactor containing 100-200 mL toluene; after stirring for 20-30 min,

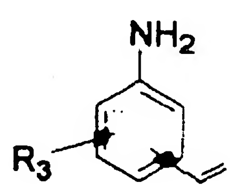
3.3-6.6 g of a polyaldehyde are added, heating is carried out at 100 ± 0.5°C for reflux for 8-12 h; the reaction mixture is acidified by 10% hydrochloric acid to pH = 1-2, extraction with ethyl ether is carried out 3-5 times, followed by washing with 30 mL saturated aqueous table salt solution and then it is dried for 12 h over anhydrous sodium sulfate; rotary evaporation is then carried out to remove the solvent and a crude product is obtained; the crude product is separated and purified by steam distillation, recrystallization or silica gel chromatography to obtain an oily liquid or a solid powder with a yield of 51-87%.

b. Preparation of substituted salicylaldehyde

0.09 mol salicylaldehyde is dissolved in 0.45 mol acetic acid, the temperature of the ice water bath is maintained below 5°C, 0.135 mol fuming sulfuric acid is added dropwise over 8 h; this is stirred overnight, the temperature is then increased slowly to 45°C. After the reaction is carried out for 5 h, cooling and filtration are carried out and the filtrate is washed three times with ice water to obtain 10.6 g of a light-yellow mixture of 3-nitro-2-hydroxybenzaldehyde and 5-nitro-2-hydroxybenzaldehyde with a yield of 95%. 6.6 g of the above mixture are added slowly to a mixed solution of 3.86 mL concentrated sulfuric acid, that has been cooled in an ice and calcium chloride bath, and 7.72 mL fuming sulfuric acid, reaction is carried out for 30 min until the light-yellow powder is completely dissolved, and a reddish-brown viscous reaction product is obtained which is poured onto a block of ice to precipitate a large amount of lemon-yellow solids, then filtration is carried out, followed by recrystallization from benzene to obtain 7.7 g of pure product 3,5-dinitro-2-hydroxybenzaldehyde with a yield of 86%.

2) Preparation of ethylene-substituted aromatic amine

The structure of the above is:

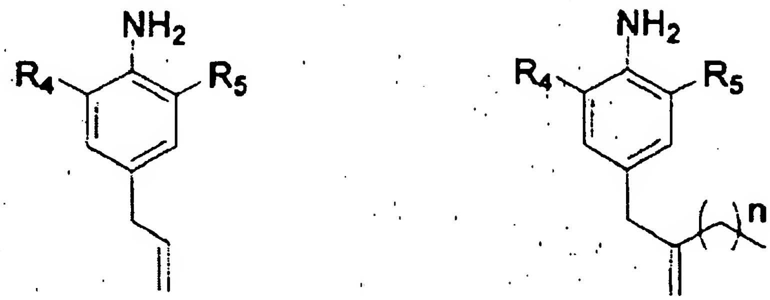


In the absence of oxygen and water, 51-74 mmol methyl triphenyl phosphorus bromide and 51-78 mmol n-butyl lithium are added to 50-70 mL of dry tetrahydrofuran, cooled with ice water, as the solvent, to carry out a reaction for 30-60 min. 50-74 mmol of a nitro aromatic aldehyde are then added to carry out a reaction for 12-18 h, the resulting mixture is washed with salt solution, extracted with chloroform, dried over anhydrous sodium sulfate and then concentrated under vacuum. The remaining solution is purified by silica gel chromatography, the eluent is toluene:ethane 1:1, and a nitro aromatic ethylene is obtained with a yield of 72-89%. A

reduction reaction is then carried out using the ion – acetic acid – ethyl alcohol system to obtain an olefin aromatic amine with a yield of 56-60%.

3) Preparation of allyl aromatic amine

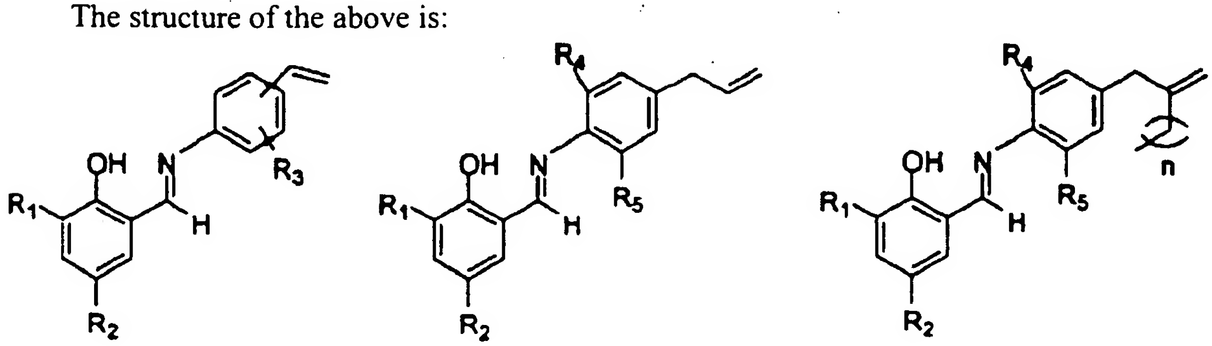
The structure of the above is:



0.1-0.2 mol aromatic amine and 0.05-0.1 mol alkenyl chloride or alkenyl bromide are heated to carry out a reflux reaction for 8-10 h, left standing to cool overnight, and then poured into 200-400 mL water. The solution is alkalized with a sodium hydroxide solution, extracted with chloroform, the pressure is reduced to a vacuum followed by distillation to obtain a N-olefin aniline with a yield of 30-84%; 0.05-0.2 mol N-olefin aromatic amine and 0.05-0.2 mol anhydrous zinc chloride are added to 50-200 mL toluene as the solvent, reflux is carried out in an argon atmosphere for 5-8 h, and after cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution, dried over anhydrous magnesium sulfate, the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain a 4-allyl aromatic amine with a yield of 25-71%.

4) Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

The structure of the above is:



In an inert gas atmosphere, using 10-30 mL methyl alcohol or ethyl alcohol as the solvent and 1 drop of 2 mL formic acid as the catalyst, a reaction is carried out between 2 mmol substituted salicylaldehyde or substituted o-hydroxyphenyl aromatic methyl ketone and 2.1 mol olefin aromatic amine at a certain temperature for 8-72 h, the mixture from the reaction is cooled, filtered, washed with cold methyl alcohol or ethyl alcohol, dried under vacuum to obtain a yellow o-hydroxylimide nitrogen and oxygen bidentate ligand with a yield of 70-90%.

5) Preparation of catalyst component A

In the absence of oxygen and water, 1.5 mmol o-hydroxylimide nitrogen and oxygen bidentate ligand are dissolved in 50 mL tetrahydrofuran, the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 4-8 h. Filtration then is carried out and the solvent is removed under vacuum to obtain a ligand sodium salt; the above sodium salt is then dissolved in a benzene solution, gradually added dropwise to a benzene solution in which 1.44 mmol trans-[$Ni(Ph)Cl(PPh_3)_2$] are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent, washing twice with n-ethane, and drying under vacuum to obtain a powdery solid catalyst with a yield of 74-87%.

6) Ethylene polymerization

In the absence of oxygen and water, using 120 mL toluene or n-ethane as a solvent, 10-65 μmol catalyst and, optionally, an auxiliary catalyst, [$Ni(COD)_2$] or [$B(C_6H_5)_3$] at twice the amount, are added to a 500-mL glass reactor; after the gas is purged three times, a polymerization reaction is carried out at room temperature and 2-7 atm of ethylene pressure for 50 min to 1.5 h while stirring; a methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain the product. The catalyst activity is 10^5 g PE/(mol•Ni•h).

The application examples provided by the present invention are as follows:

Application Example 1 Preparation of the substituted salicylaldehyde

In an argon atmosphere, 0.1 mol substituted 4-methoxyl-phenol, 0.01 mol tin tetrachloride and 0.04 mol triethylamine are added to a reactor containing 200 mL toluene. After stirring for 20 min, 6.6 g of a polyaldehyde are added, heating is carried out at 100 ± 0.5°C for reflux for 10 h; the reaction mixture is acidified by 10% hydrochloric acid to pH = 1, extraction with ethyl ether is carried out 3 times, followed by washing with 30 mL saturated aqueous table salt solution and then it is dried for 12 h over anhydrous sodium sulfate; rotary evaporation is then carried out to remove the solvent and a crude product is obtained; the crude product is

recrystallized from petroleum ether to obtain 7.8 g of 5-methoxy-2-salicylaldehyde. The yield is 51%.

Application Example 2 Preparation of the substituted salicylaldehyde

In an argon atmosphere, 0.05 mol o-hydroxy phenol, 0.005 mol tin tetrachloride and 0.02 mol 2,6-dimethyl piridine are added to a reactor containing 100 mL toluene. After stirring for 20 min, 3.3 g of polyaldehyde are added, heating is carried out at 100 ± 0.5°C for reflux for 8 h; the reaction mixture is acidified by 10% hydrochloric acid to pH = 2, extraction with ethyl ether is carried out 5 times, followed by washing with 30 mL saturated aqueous table salt solution and then it is dried for 12 h over anhydrous sodium sulfate; rotary evaporation is then carried out to remove the solvent and a crude product is obtained; the crude product is purified by silica gel chromatography with the eluent being ethane:chloroform 1:1 to obtain 6.3 g of 3-phenyl-2-salicylaldehyde as a light-yellow solid powder with a yield of 64%.

Application Example 3 Preparation of the substituted salicylaldehyde*

...0.178 mol iron powder, the mixed solution is refluxed for 1 h under the protection of argon, cooled to room temperature, poured into 350 mL water, neutralized by solid sodium carbonate to neutrality, the thick solution is extracted with ethyl ether, concentrated under vacuum, a small amount of p-biphenyl benzene is added to the remaining solution, the pressure is reduced and distillation is carried out to obtain 3.2 g of a colorless liquid, o-aminostyrene, with a yield of 60.0%.

Application Example 6 Preparation of ethylene aromatic amine

The operation is the same as in Application Example 5, except the amount of the m-nitroaldehyde is 50 mmol and 2.17 g of m-aminostyrene are obtained with a yield of 41.5%.

Application Example 7 Preparation of ethylene aromatic amine

The operation is the same as in Application Example 5, except the amount of the p-nitroaldehyde is 50 mmol and 3.02 g of p-aminostyrene are obtained with a yield of 50.7%.

Application Example 8 Preparation of ethylene aromatic amine

74 mmol methyltriphenylphosphorus bromide are dissolved in 70 mL dry tetrahydrofuran cooled by ice water in an argon atmosphere, and then 48.8 mL 1.6 M n-butyl lithium are added

* [Translator's note: p.7 is omitted from the original document.]

to the resulting product. 50 min, later 100 mL tetrahydrofuran solution, in which 74 mmol 3-nitro-4-methylaldehyde are dissolved, are added and stirred to carry out a reaction for 16 h, which is followed by washing with salt solution and extraction with chloroform. The extraction solution is dried over anhydrous sodium sulfate, concentrated under vacuum, the remaining solution is purified by silica gel chromatography, the eluent is toluene:ethane 1:1 and 8.68 g of a yellow liquid, 3-nitro-4-methylstyrene, are obtained with a yield of 72.0%. 45 mmol of the obtained o-nitrostyrene are dissolved in a mixed solution of 50 mL glacial acetic acid and 50 mL anhydrous ethyl alcohol to which 0.178 mol iron powder is added. The mixed solution is refluxed for 1 h under the protection of argon, cooled to room temperature, poured into 350 mL water, neutralized by solid sodium carbonate to neutrality, then the thick solution is extracted with ethyl ether, concentrated under vacuum, and a small amount of p-biphenylbenzene is added to the remaining solution. The pressure is reduced and distillation is carried out to obtain 3.41 g of a colorless liquid, 3-amino-4-methylstyrene with a yield of 57%.

Application Example 9 Preparation of ethylene aromatic amine

60 mmol methyltriphenylphosphorus bromide are dissolved in 60 mL dry tetrahydrofuran cooled by ice water in an argon atmosphere, and then 37.5 mL 1.6M n-butyllithium are added to the resulting product. 60 min later, 100 mL tetrahydrofuran solution, in which 60 mmol 3-isopropyl-4-nitroaldehyde [transliteration] are dissolved, are added and stirred to carry out a reaction for 18 h, which is followed by washing with salt solution, extraction with chloroform, the extraction solution is dried over anhydrous sodium sulfate, concentrated under vacuum, the remaining solution is purified by silica gel chromatography, the eluent is toluene:ethane 1:1, and 9.11 g of a yellow liquid, 3-isopropyl 4-nitrostyrene, are obtained with a yield of 79.5%.
45 mmol of the obtained o-nitrostyrene are dissolved in a mixed solution of 50 mL glacial acetic acid and 50 mL anhydrous ethyl alcohol to which 0.178 mol iron powder is added, the mixed solution is refluxed for 1 h under the protection of argon, cooled to room temperature, poured into 350 mL water, neutralized by solid sodium carbonate to neutrality, the thick solution is extracted with ethyl ether, concentrated under vacuum, a small amount of p-biphenyl benzene is added to the remaining solution, the pressure is reduced and distillation is carried out to obtain 4.06 g of a colorless liquid, 3-isopropyl-4-aminostyrene with a yield of 56.0%.

Application Example 10 Preparation of allyl aromatic amine

0.2 mol 2,6-diisopropylaniline and 0.1 mol allyl hydrocarbon [sic] chloride are heated to carry out reaction at reflux for 8 h, left standing to cool overnight, and then poured into 400 mL water, the solution is alkalized with a sodium hydroxide solution, extracted with chloroform, the pressure is reduced to a vacuum followed by distillation to obtain 18.33 g N-allyl hydrocarbon-

2,6-diisopropylaniline with a yield of 84%. 100 mL toluene are used as the solvent, 0.084 mol N-allyl hydrocarbon-2,6-diisopropylaniline and 0.1 mol anhydrous zinc chloride are added and reflux is carried out in an argon atmosphere for 5 h. After cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution, dried with anhydrous magnesium sulfate, and the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain 12.92 g 4-allyl hydrocarbon-2,6-diisopropylaniline with a yield of 71%.

Application Example 11 Preparation of allyl aromatic amine

0.1 mol 2-tert-butylaniline and 0.05 mol of a 1-bromo-2-butyl olefin are heated to carry out a reflux reaction for 10 h, left standing to cool overnight, and then poured into 200 mL water, the solution is alkalized with a sodium hydroxide solution, extracted with chloroform, and the pressure is reduced to a vacuum followed by distillation to obtain 5.35 g N-(2-methylethylene)-2-tert-butylaniline with a yield of 53%. 200 mL toluene are used as the solvent, 0.2 mol N-(2-methylethylene)-2-tert-butylaniline and 0.2 mol anhydrous zinc chloride are added, reflux is carried out in an argon atmosphere for 8 h. After cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution, dried with anhydrous magnesium sulfate, the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain 24.89 g 4-(2-methylethylene)-2-tert-butylaniline with a yield of 61%.

Application Example 12 Preparation of allyl aromatic amine

0.12 mol 2,6-dimethylaniline and 0.06 mol 1-bromo-2-pentadiene are heated to carry out a reflux reaction for 9 h, left standing to cool overnight, and then poured into 300 mL water. The solution is alkalized with a sodium hydroxide solution, extracted with chloroform, the pressure is reduced to a vacuum followed by distillation to obtain 3.72 g N-(2-ethylethylene)-2,6-dimethylaniline with a yield of 33%. 0.05 mol N-(2-ethylethylene)-2,6-dimethylaniline and 0.05 mol anhydrous zinc chloride are added to 80 mL toluene are used as the solvent, reflux is carried out in an argon atmosphere for 7 h, and after cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution, dried with anhydrous magnesium sulfate, the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain 2.77 g 4-allyl hydrocarbon-2,6-diisopropylaniline with a yield of 29%.

Application Example 13 Preparation of allyl aromatic amine

0.1 mol 2,6-diisopropylaniline and 0.05 mol 1-bromo-2-heptene are heated to carry out a reflux reaction for 10 h, left standing to cool overnight, and then poured into 300 mL water. The solution is alkalized with a sodium hydroxide solution and extracted with chloroform, the pressure is reduced to a vacuum followed by distillation to obtain 4.09 g N-(2-butyl ethylene)-2,6-diisopropylaniline with a yield of 30%. 0.05 mol N-(2-butyl ethylene)-2,6-diisopropylaniline and 0.05 mol anhydrous zinc chloride are added to 50 mL toluene as the solvent, reflux is carried out in an argon atmosphere for 8 h, and after cooling, the solution is poured into a sodium hydroxide solution to alkalize it, the organic layer is separated, the insoluble substances at the bottom are dissolved in hot concentrated hydrochloric acid and then poured into the above ethyl ether extraction solution and dried with anhydrous magnesium sulfate, the pressure is reduced and it is concentrated under vacuum followed by distillation to obtain 3.44 g 4-(2-butyl allyl hydrocarbon)-2,6-diisopropylaniline with a yield of 25%.

Application Example 14 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

In a nitrogen atmosphere, using 10 mL ethyl alcohol as the solvent and 2 drops of formic acid as the catalyst, a reaction is carried out between 20 mmol salicylaldehyde and 21 mol 2-ethyleneaniline [sic; possibly 2-ethylaniline] at room temperature for 36 h, the mixture from the reaction is cooled, filtered, washed with cold ethyl alcohol, and dried under vacuum to obtain 3.1 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{15}H_{13}NO$ with a yield of 70%.

Application Example 15 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

In a nitrogen atmosphere, using 15 mL methyl alcohol as the solvent and 2 drops of formic acid as the catalyst, a reaction is carried out between 20 mmol 5-methyl-3-tert-butyl-2-salicylaldehyde and 21 mol 3-amino-4-methylaniline at room temperature for 36 h, the mixture from the reaction is cooled, filtered, washed with cold methyl alcohol, and dried under vacuum to obtain 4.4 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{20}H_{25}NO$ with a yield of 75%.

Application Example 16 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

In a nitrogen atmosphere, using 10 mL methyl alcohol as the solvent and 3 drops of formic acid as the catalyst, a reaction is carried out between 20 mmol 3,5-dinitro-2-

salicylaldehyde and 21 mol 4-allyl-2,6-diisopropylaniline at room temperature for 40 h, the mixture from the reaction is cooled, filtered, washed with cold methyl alcohol, and dried under vacuum to obtain 5.8 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{22}H_{25}N_3O_5$ with a yield of 70%.

Application Example 17 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

In a nitrogen atmosphere, using 20 mL ethyl alcohol as the solvent and 0.2 mL formic acid as the catalyst, a reflux reaction is carried out between 20 mmol 3-phenyl-2-salicylaldehyde and 21 mol 4-allyl hydrocarbon-2,6-dimethylaniline for 8 h, the mixture from the reaction is cooled, filtered, washed with cold ethyl alcohol, and dried under vacuum to obtain 5.7 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{24}H_{23}NO$ with a yield of 83%.

Application Example 18 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

The operation is carried out as in Application Example 17, and a reflux reaction between 20 mmol 3-phenyl-2-salicylaldehyde and 21 mol 4-allyl hydrocarbon-2,6-diisopropylaniline for 8 h to obtain 6.5 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{26}H_{27}NO$ with a yield of 82%.

Application Example 19 Preparation of o-hydroxylimide nitrogen and oxygen bidentate ligand containing an olefin group

In a nitrogen atmosphere, using 20 mL methyl alcohol as the solvent and 0.2 mL formic acid as the catalyst, a reaction is carried out between 2.0 mmol 3-(9-anthroic)-2-salicylaldehyde and 2.1 mol 4-(2-ethyl) allyl hydrocarbon-2,6-diisopropylaniline at room temperature for 20 h, the mixture from the reaction is cooled, filtered, washed with cold methyl alcohol or ethyl alcohol, and dried under vacuum to obtain 8.7 g of a yellow o-hydroxyl aromatic imide bidentate ligand $C_{35}H_{35}NO$ with a yield of 89%.

Application Example 20 Preparation of catalyst component A

In the absence of oxygen and water, 1.5 mmol of the o-hydroxyl aromatic imide nitrogen and oxygen bidentate ligand $C_{15}H_{13}NO$ obtained in Application Example 14 are dissolved in 50 mL tetrahydrofuran, and the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 4 h. Afterwards filtration is carried out and the solvent is removed under vacuum to obtain a ligand sodium salt. The sodium salt is then dissolved in a 30 mL benzene solution, gradually added dropwise to 50 mL of a benzene solution in which 1.44 mmol trans-

$[Ni(Ph)Cl(PPh_3)_2]$ are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent and drying to obtain 0.78 g of a powdery solid catalyst $C_{45}H_{43}NOPNi$ with a yield of 74%.

Application Example 21 Preparation of catalyst component A

In the absence of oxygen and water, 1.5 mmol of the o-hydroxyl aromatic imide nitrogen and oxygen bidentate ligand $C_{26}H_{27}NO$ obtained in Application Example 18 are dissolved in 50 mL tetrahydrofuran, and the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 8 h. Filtration is then carried out, and the solvent is removed under vacuum to obtain a ligand sodium salt. The sodium salt is then dissolved in a 40 mL benzene solution, gradually added dropwise to 50 mL of a benzene solution in which 1.44 mmol trans-$[Ni(Ph)Cl(PPh_3)_2]$ are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent and drying to obtain 0.84 g of a powdery solid catalyst $C_{52}H_{49}NOPNi$ with a yield of 71%.

Application Example 22 Preparation of catalyst component A

In the absence of oxygen and water, 1.5 mmol of the o-hydroxyl aromatic imide nitrogen and oxygen bidentate ligand $C_{22}H_{25}N_3O_5$ obtained in Application Example 16 are dissolved in 50 mL tetrahydrofuran, and the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 6 h. Afterwards filtration is carried out, and the solvent is removed under vacuum to obtain a ligand sodium salt. The sodium salt is dissolved in a 50 mL benzene solution, gradually added dropwise to 50 mL of a benzene solution in which 1.44 mmol trans-$[Ni(Ph)Cl(PPh_3)_2]$ are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent and drying to obtain 0.88 g of a powdery solid catalyst $C_{45}H_{41}N_3O_5PNi$ with a yield of 77%.

Application Example 23 Preparation of the catalyst component A

In the absence of oxygen and water, 1.5 mmol of the o-hydroxyl aromatic imide nitrogen and oxygen bidentate ligand $C_{35}H_{35}NO$ obtained in Application Example 19 are dissolved in 50 mL tetrahydrofuran, and the solution is added to 5.0 mmol sodium hydride to carry out a reaction for 6 h. Filtration is carried out, and the solvent is removed under vacuum to obtain a ligand sodium salt. Then the sodium salt is dissolved in 40 mL of a benzene solution, gradually added dropwise to 50 mL of a benzene solution in which 1.44 mmol trans-$[Ni(Ph)Cl(PPh_3)_2]$ are dissolved to carry out a reaction for 12 h, and then filtration is carried out, followed by concentration under vacuum to remove the solvent and drying to obtain 0.94 g of a powdery solid catalyst $C_{65}H_{59}NOPNi$ with a yield of 65%.

Application Example 24 Ethylene polymerization

In the absence of oxygen and water, 120 mL toluene and 65 μmol of the catalyst $C_{52}H_{49}NOPNi$ obtained in Application Example 21 are added to a 500-mL glass reactor, and after the gas is purged three times, a polymerization reaction is carried out at room temperature and 4 atm of ethylene pressure for 1 h. A methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain 10.9 g of polymer. The catalyst activity is 2.0×10^5 g PE/(mol•Ni•h).

Application Example 25 Ethylene polymerization

The operation is carried out as in Application Example 24, except the polymerization reaction is carried out under 2 atm of ethylene pressure for 2 h to obtain 12.2 g of polymer. The catalyst activity is 0.9×10^5 g PE/(mol•Ni•h).

Application Example 26 Ethylene polymerization

In the absence of oxygen and water, 120 mL toluene, 65 μmol of the catalyst $C_{45}H_{43}NOPNi$ obtained in Application Example 20 and 130 μmol $Ni(COD)_2$ as an auxiliary catalyst are added to a 500-mL glass reactor, and after the gas is purged three times, a polymerization reaction is carried out at room temperature and 7 atm of ethylene pressure for 50 min. A methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain 14.6 g of polymer. The catalyst activity is 2.1×10^5 g PE/(mol•Ni•h).

Application Example 27 Ethylene polymerization

In the absence of oxygen and water, 120 mL toluene and 33 μmol of the catalyst $C_{52}H_{49}NOPNi$ obtained in Application Example 21 are added to a 500-mL glass reactor, and after the gas is purged three times, a polymerization reaction is carried out at room temperature and 3 atm of ethylene pressure for 1.5 h. A methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain 2.1 g of polymer. The catalyst activity is 0.45×10^5 g PE/(mol•Ni•h).

Application Example 28 Ethylene polymerization

In the absence of oxygen and water, 120 mL n-ethane and 10 μmol of the catalyst $C_{52}H_{49}NOPNi$ obtained in Application Example 21 are added to a 500-mL glass reactor, and after the gas is purged three times, a polymerization reaction is carried out at room temperature and 7 atm of ethylene pressure for 1 h. A methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain 2.3 g of polymer. The catalyst activity is 1.1×10^5 g PE/(mol•Ni•h).

Application Example 29 Ethylene polymerization

In the absence of oxygen and water, 120 mL toluene, 65 μmol of the catalyst $C_{45}H_{43}NOPNi$ obtained in Application Example 20 and 130 μmol pentafluorophenyl borane [$B(C_6F_5)_3$] as an auxiliary catalyst are added to a 500-mL glass reactor, and after the gas is purged three times, a polymerization reaction is carried out at room temperature and 7 atm of ethylene pressure for 50 min. A methyl alcohol solution containing 10% hydrochloric acid is used to terminate the reaction, the obtained polymer is filtered, washed with methyl alcohol three times, and then it is dried under vacuum at 40°C for 24 h to obtain 14.6 g of polymer. The catalyst activity is 2.0×10^5 g PE/(mol•Ni•h).

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[71]申请人 中国科学院长春应用化学研究所

地址 130022 吉林省长春市人民大街159号

[72]发明人 金国新 张 道

[74]专利代理机构 长春科宇专利代理有限责任公司

代理人 曹桂珍

权利要求书4页 说明书15页 附图页数0页

[54]发明名称 自固载化的"茂后"镍基烯烃聚合催化剂的制备方法

[57]摘要

本发明是关于自固载化后过渡金属"茂后"烯烃聚合催化剂 的制备。催化剂由A单组分或A和B双组分组成,A组分表达式 为[Comp(M-ANO)],Comp表示配合物,M表示后过渡金属镍,ANO表示烯烃基取代的邻羟基亚胺类氮、氧双齿配体。B组分为环辛二烯 合镍$[Ni(COD)_2]$或五氟苯硼$[B(C_6F_5)_3]$。这类催化剂催化乙烯聚合具有 较高的催化活性,最重要的是这类催化剂可以不需要助催化剂。

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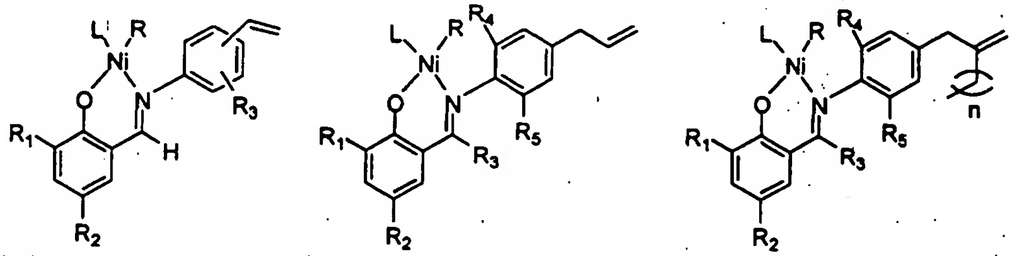
权 利 要 求 书

1．一种自固载化的“茂后”镍基烯烃聚合催化剂的制备方法，其特征在于制备的催化剂由A单组分或A和B双组分组成，A组分表达式为[Comp(M-ANO)], Comp表示配合物，M表示后过渡金属镍，ANO表示烯烃基取代的水杨醛亚胺类氮、氧双齿配体；

具体结构如下：

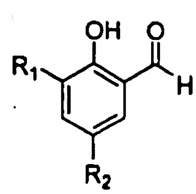


其中 R_1, R_2 为 H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen, Anth, Trityl, TPhen, OMe, NO_2 其中任意一种；R_3, R_4, R_5 为 H, Me, ^{i}Pr, ^{t}Bu 其中任意一种；R = Ph, L = PPh_3; n = 0, 1, 2, 3, 4; B组分为环辛二烯合镍[$Ni(COD)_2$]或五氟苯硼[$B(C_6F_5)_3$]其中任意一种；

催化剂的制备过程如下：

1）a. 取代的邻羟基苯甲醛的制备

其结构式为



在惰性气氛下，向装有 100~200 毫升的甲苯的反应器中加入 0.05~0.1 摩尔取代苯酚、0.005~0.01 摩尔催化剂四氯化锡和 0.02-0.04 摩尔有机胺，具体为三乙基胺、三丁基胺和吡啶；搅拌 20-30 分钟后

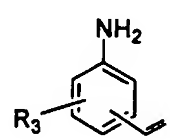
在加入 3.3~6.6 克多聚甲醛，在 100±0.5℃加热回流 8~12 小时；反应混合物经 10%的盐酸酸化至 PH=1-2、乙醚萃取 3-5 次、30 毫升饱和食盐水洗涤和无水硫酸钠干燥 12 小时后，旋转蒸发去除溶剂得粗产品；粗产品经水蒸气蒸馏、重结晶或硅胶柱层析分离提纯得到油状液体或固体粉末，产率 51~87%；

b.取代的邻羟基苯甲醛的制备

将水杨醛 0.09mol 溶于 0.45mol 乙酸中，冰水浴控制温度低于 5℃，8 小时内滴加 0.135mol 发烟硝酸摩尔，搅拌过夜，缓慢升温至 45℃，反应 5 小时后，冷却，过滤，滤饼用冰水洗涤 3 次，得到淡黄色 3-硝基-2-羟基苯甲醛和 5-硝基-2-羟基苯甲醛的混合物 10.6 克，产率 95%，取上述混合物 6.6 克慢慢加入用冰-氯化钙浴冷却的浓硫酸 3.86ml 和发烟硝酸 7.72ml 的混合液中，反应 30 分钟，淡黄色粉末全部溶解，将红棕色粘稠状反应物倒入冰块上，析出大量柠檬黄固体，过滤用苯重结晶得纯品 3,5-二硝基-2-羟基苯甲醛 7.7 克，产率 86%；

2）乙烯基取代芳胺的制备

其结构式为：

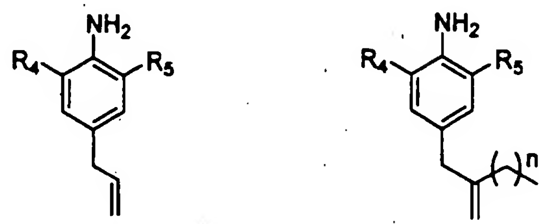


在无氧无水的条件下，以干燥的四氢呋喃 50-70 毫升为溶剂，冰水冷却，加入 51-74 毫摩尔甲基三苯基溴化鏻与 51-78 毫摩尔正丁基锂进行反应，30-60 分钟后，加入硝基芳甲醛 50-74 毫摩尔，反应 12-18 小时，所得混合液经盐水洗涤，三氯甲烷萃取，无水硫酸钠干燥后真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得硝基芳乙烯，产率 72－89%，再经过铁－醋酸

一乙醇体系还原制得烯烃基芳胺，产率 56－60％；

3)烯丙基类芳胺的制备

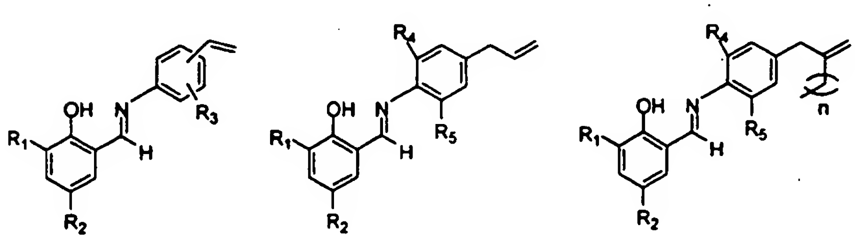
其结构式为:



将芳胺 0.1-0.2 摩尔和烯烃基氯基或烯烃基溴 0.05-0.1 摩尔加热回流 8-10 小时,冷却放置过夜,倾入 200-400 毫升水中,用氢氧化钠溶液碱化,乙醚萃取,真空减压蒸馏得 N-烯烃基苯胺，产率 30~84%;以 50-200 毫升甲苯为溶剂加入 N-烯烃基芳胺 0.05-0.2 摩尔和无水氯化锌 0.05-0.2 摩尔,氩气气氛下回流 5-8 小时,冷却后倾入氢氧化钠水溶液中碱化,分离出有机层,下层不溶物溶于热的浓盐酸中,再倾入上述乙醚萃取液中,无水硫酸镁干燥,真空浓缩后减压蒸馏得 4-烯丙基类芳胺，产率 25-71%;

4)含有烯烃基团的邻羟基芳亚胺类氮氧双齿配体的制备

其结构式为:



在惰性气氛下,以 10-30 毫升甲醇或乙醇为溶剂,1 滴-2 毫升甲酸为催化剂,2 毫摩尔取代的邻羟基苯甲醛与 2.1 摩尔烯烃基芳胺在室温下反应 8-72 小时,反应混合物冷却,过滤,用冷的甲醇或乙醇洗涤,真空干燥得黄色邻羟基芳亚胺类氮氧双齿配体，产率为 70-90%;

5）催化剂 A 组分的制备

在无水无氧条件下，1.5 毫摩尔邻羟基芳亚胺类氮氧双齿配体溶解于 50 毫升四氢呋喃，加到 5.0 毫摩尔氢化钠中反应 4-8 小时后，过滤，真空除去溶剂得配体钠盐；再将上述钠盐溶于苯溶剂中，慢慢滴加到溶有 1.44 毫摩尔 trans-$[Ni(Ph)Cl(PPh_3)_2]$的苯溶液中，反应 12 小时后过滤，真空浓缩除去溶剂，正己烷洗涤 2 次，真空干燥得粉末状催化剂固体，产率 74-87%;

6)乙烯聚合

无氧无水条件下，在 500ml 玻璃反应釜中加人 120ml 溶剂甲苯或正己烷，10-65μmol 的催化剂，加入或不加入 2 倍量的助催化剂 $Ni(COD)_2$或 $B(C_6H_5)_3$），换气三次后，保持在室温和 2-7atm 的乙烯压力下搅拌聚合 50 分钟到 1.5 小时；用含 10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤 3 次，并于 40℃真空干燥 24 小时，得聚合物，催化效率为 10^5g PE/(mol·Ni·hr)。

2.如权利要求 1 所述的自固载化的“茂后”镍基烯烃聚合催化剂的制备方法，其特征在于所述催化剂体系中 R_1, R_2 为 H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen，NO_2。

说 明 书

自固载化的“茂后”镍基烯烃聚合催化剂的制备方法

本发明属于含有烯烃基团的自固载化“茂后”后过渡金属烯烃聚合催化剂的制备方法。

作为最重要的一类高分子材料，聚烯烃的存在大大改善了人类的生存环境和生活条件。烯烃在催化剂的作用下形成聚合物，改变催化剂的结构可以得到特定分子结构和特定性能的聚烯烃产物，因而催化剂成为聚烯烃升级换代、不断进步的核心和原动力。起始于上个世纪末的“茂后”后过渡金属催化剂是继 Ziegler-Natta 催化剂和茂金属催化剂之后的新一代高活性烯烃聚合催化剂，现已成为世界范围内新型烯烃聚合催化剂的研究热点。后过渡金属催化剂是后过渡金属镍、钯、铁、钴等的金属有机化合物。这类催化剂不仅活性高，价廉易得，能够催化乙烯及α-烯烃聚合得到高分子量的聚合物，而且还能催化极性单体与烯烃的共聚，这是前两代催化剂所不具备的。欧美各国以及 Du Pont 公司和 B.P. Chemistry 公司均投入大量资金进行研究和开发。

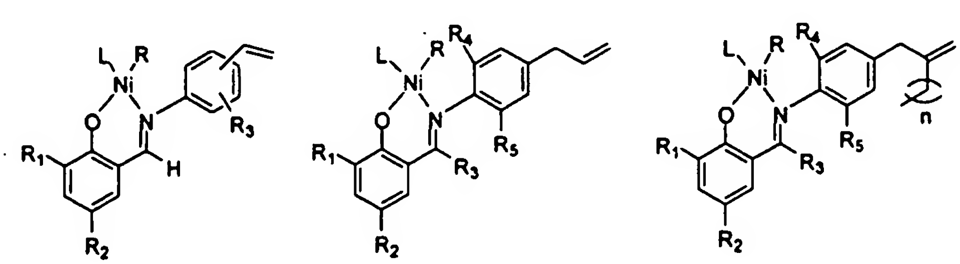
前不久，美国 Grubbs 研究小组（*Science*, 2000, 287, 460-462; *Organometallics*, 1998, 17, 3149-3151）报道了一类新型单组分中性镍烯烃聚合催化剂，这类催化剂不仅表现出高活性，能产生高分子量聚乙烯，而且对氧、氮和硫等杂原子表现出非凡的容忍能力强，可以与极性单体共聚。最为引人注目的是这类后过渡烯烃聚合催化剂可

以不需要 MAO、Ni(COD)$_2$类助催化剂。因此它对起始原料单体纯度的要求大大降低，更有利于工业化生产。同时，这一开创性工作为聚合带有极性官能团的烯烃，生产具有特殊性能,如可生物降解，表面改性的聚合物打开了方便之门。这类催化剂的自固载化工作至尽未见报道，为了实现这类催化剂的可控聚合，提高催化活性，得到理想分子量和支化度的聚合物，适应工业化生产装置，自固载化的工作有一定的意义。

本发明的目的是提供一种自固载化的“茂后”烯烃聚合催化剂的制备方法。该方法采用含有烯烃取代基团的芳胺与取代水杨醛缩合成氮氧双齿有机配体，再与镍的烷基化合物作用，形成含有烯烃基团的自固载“茂后”后过渡金属烯烃聚合催化剂。

自固载化的“茂后”后过渡金属烯烃聚合催化剂在催化烯烃聚合的过程中，烯烃和催化剂上的烯烃基会发生共聚，使催化剂相当于固载在聚烯烃链上，这样可以最大限度地发挥活性中心的催化作用。聚合实验表明其对烯烃聚合的活性较高，可以为非自固载同类催化剂的几倍到几十倍。

本发明制备的催化剂由 A 单组分或 A 和 B 双组分组成，A 组分表达式为[Comp(M-ANO)], Comp 表示配合物，M 表示后过渡金属镍，ANO 表示烯烃基取代的水杨醛亚胺类氮、氧双齿配体。具体结构如下：

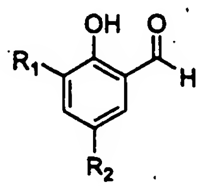


其中 R_1, R_2 为 H, Me, ^{i}Pr, ^{t}Bu, Ph, Phen, Anth, Trityl, TPhen, OMe, NO_2 其中任意一种；R_3, R_4, R_5 为 H, Me, ^{i}Pr, ^{t}Bu 其中任意一种；R = Ph, L = PPh_3; n = 0, 1, 2, 3, 4; B 组分为环辛二烯合镍[$Ni(COD)_2$]或五氟苯硼[$B(C_6F_5)_3$]其中任意一种。

催化剂的制备过程如下：

1）a. 取代的邻羟基苯甲醛的制备

其结构式为



在惰性气氛下，向装有 100~200 毫升的甲苯的反应器中加入 0.05~0.1 摩尔取代苯酚、0.005~0.01 摩尔催化剂四氯化锡和 0.02-0.04 摩尔有机胺，具体为三乙基胺、三丁基胺和吡啶等。搅拌 20-30 分钟后在加入 3.3~6.6 克多聚甲醛，在 100±0.5℃加热回流 8~12 小时。反应混合物经 10%的盐酸酸化至 PH=1-2、乙醚萃取 3-5 次、30 毫升饱和食盐水洗涤和无水硫酸钠干燥 12 小时后，旋转蒸发去除溶剂得粗产品。粗产品经水蒸气蒸馏、重结晶或硅胶柱层析分离提纯得到油状液体或固体粉末。产率 51~87%。

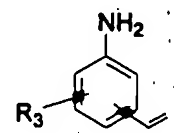
b.取代的邻羟基苯甲醛的制备

将水杨醛 0.09mol 溶于 0.45mol 乙酸中，冰水浴控制温度低于 5℃，8 小时内滴加 0.135mol 发烟硝酸摩尔，搅拌过夜，缓慢升温至 45℃，反应 5 小时后，冷却，过滤，滤饼用冰水洗涤 3 次，得到淡黄色 3-硝基-2-羟基苯甲醛和 5-硝基-2-羟基苯甲醛的混合物 10.6 克．产率 95%．取上述混合物 6.6 克慢慢加入用冰-氯化钙浴冷却的浓硫酸 3.86ml 和

发烟硝酸 7.72ml 的混合液中，反应 30 分钟，淡黄色粉末全部溶解，将红棕色粘稠状反应物倒入冰块上，析出大量柠檬黄固体，过滤用苯重结晶得纯品 3,5-二硝基-2-羟基苯甲醛 7.7 克. 产率 86%.

2）乙烯基取代芳胺的制备

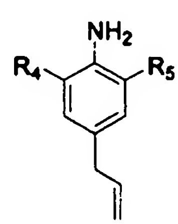
其结构式为：

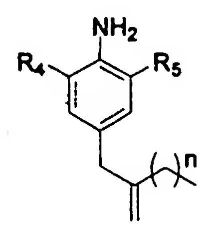


在无氧无水的条件下，以干燥的四氢呋喃 50-70 毫升为溶剂，冰水冷却，加入 51-74 毫摩尔甲基三苯基溴化鏻与 51-78 毫摩尔正丁基锂进行反应，30-60 分钟后，加入硝基芳甲醛 50-74 毫摩尔，反应 12-18 小时，所得混合液经盐水洗涤，三氯甲烷萃取，无水硫酸钠干燥后真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得硝基芳乙烯，产率 72－89%，再经过铁一醋酸一乙醇体系还原制得烯烃基芳胺，产率 56－60%；

3)烯丙基类芳胺的制备

其结构式为：



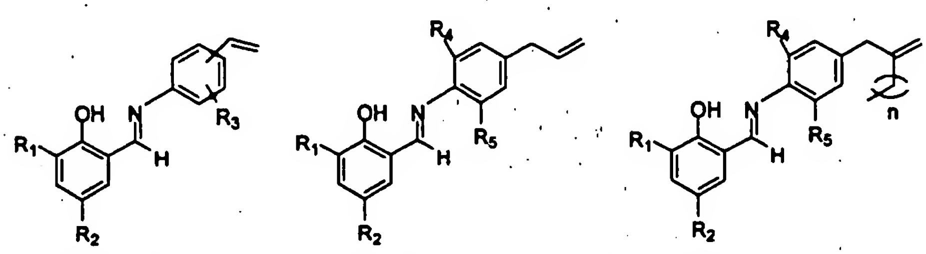


将芳胺 0.1-0.2 摩尔和烯烃基氯基或烯烃基溴 0.05-0.1 摩尔加热回流 8-10 小时，冷却放置过夜，倾入 200-400 毫升水中，用氢氧化钠溶液碱化，乙醚萃取，真空减压蒸馏得 N-烯烃基苯胺. 产率 30~84%。以 50-200 毫升甲苯为溶剂加入 N-烯烃基芳胺 0.05-0.2 摩尔和无水氯化锌 0.05-0.2 摩尔，氩气气氛下回流 5-8 小时，冷却后倾入氢氧化钠水

溶液中碱化,分离出有机层,下层不溶物溶于热的浓盐酸中,再倾入上述乙醚萃取液中,无水硫酸镁干燥,真空浓缩后减压蒸馏得 4-烯丙基类芳胺.产率 25-71%.

4)含有烯烃基团的邻羟基芳亚胺类氮氧双齿配体的制备

其结构式为:



在惰性气氛下,以10-30毫升甲醇或乙醇为溶剂,1滴-2毫升甲酸为催化剂,2 毫摩尔取代的邻羟基苯甲醛或取代的邻羟基苯基芳基甲酮与2.1摩尔烯烃基芳胺在一定温度下反应8-72小时,反应混合物冷却,过滤,用冷的甲醇或乙醇洗涤,真空干燥得黄色邻羟基芳亚胺类氮氧双齿配体.产率为70-90%.

5）催化剂A组分的制备

在无水无氧条件下，1.5毫摩尔邻羟基芳亚胺类氮氧双齿配体溶解于50毫升四氢呋喃，加到5.0毫摩尔氢化钠中反应4-8小时后，过滤，真空除去溶剂得配体钠盐。再将上述钠盐溶于苯溶剂中，慢慢滴加到溶有1.44毫摩尔 trans-$[Ni(Ph)Cl(PPh_3)_2]$的苯溶液中，反应12小时后过滤，真空浓缩除去溶剂，正己烷洗涤2次，真空干燥得粉末状催化剂固体。产率 74-87%。

6)乙烯聚合

无氧无水条件下，在500ml 玻璃反应釜中加人120ml 溶剂甲苯或正己烷，10-65μmol 的催化剂，加入或不加入 2 倍量的助催

化剂 Ni(COD)$_2$或 B(C_6H_5)$_3$)，换气三次后，保持在室温和 2-7atm 的乙烯压力下搅拌聚合 50 分钟到 1.5 小时。用含 10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤 3 次，并于 40℃真空干燥 24 小时，得聚合物，催化效率为 10^5 g PE/(mol·Ni·hr)。

本发明提供的实施例如下：

实施例 1：取代的邻羟基苯甲醛的制备

在氮气气氛下，向装有 200 毫升的甲苯的反应器中加入 0.1 摩尔 4-甲氧基-苯酚、0.01 摩尔四氯化锡和 0.04 摩尔三乙基胺。搅拌 20 分钟后在加入 6.6 克多聚甲醛，在 100±0.5℃加热回流 10 小时。反应混合物经 10%的盐酸酸化至 PH=1、乙醚萃取 3 次、30 毫升饱和食盐水洗涤和无水硫酸钠干燥 12 小时后，旋转蒸发去除溶剂得粗产品。粗产品经石油醚重结晶得 5-甲氧基-2-羟基苯甲醛 7.8 克。产率 51%。

实施例 2：取代的邻羟基苯甲醛的制备

在氮气气氛下，向装有 100 毫升的甲苯的反应器中加入 0.05 摩尔邻苯基苯酚、0.005 摩尔四氯化锡和 0.02 摩尔 2，6-二甲基吡啶。搅拌 20 分钟后在加入 3.3 克多聚甲醛，在 100±0.5℃加热回流 8 小时。反应混合物经 10%的盐酸酸化至 PH=2、乙醚萃取 5 次、30 毫升饱和食盐水洗涤和无水硫酸钠干燥 12 小时后，旋转蒸发去除溶剂得粗产品。粗产品硅胶柱层析分离，淋洗剂为己烷/氯仿 1：1，得到淡黄固体粉末 3-苯基-2-羟基苯甲醛 6.3 克。产率 64%。

实施例 3：取代的邻羟基苯甲醛的制备

在氩气气氛下，向装有150毫升的甲苯的反应器中加入0.075摩尔4-甲基-2-特丁基苯酚、0.0075摩尔四氯化锡和0.03摩尔三正丁胺。搅拌20分钟后在加入4.5克多聚甲醛，在100±0.5℃加热回流12小时。反应混合物经10%的盐酸酸化至PH=1.5、乙醚萃取4次、30毫升饱和食盐水洗涤和无水硫酸钠干燥12小时后，旋转蒸发去除溶剂得粗产品。粗产品依次经水蒸气蒸馏得到黄色油状液体5-甲基-3-特丁基-2-羟基苯甲醛12.5克。产率87%。

实施例4：取代的邻羟基苯甲醛的制备

将水杨醛0.09mol溶于0.45mol乙酸中，冰水浴控制温度低于5℃，8小时内滴加0.135mol发烟硝酸摩尔，搅拌过夜，缓慢升温至45℃，反应5小时后，冷却，过滤，滤饼用冰水洗涤3次，得到淡黄色3-硝基-2-羟基苯甲醛和5-硝基-2-羟基苯甲醛的混合物10.6克，产率95%. 取上述混合物6.6克慢慢加入用冰-氯化钙浴冷却的浓硫酸3.86ml和发烟硝酸7.72ml的混合液中，反应30分钟，淡黄色粉末全部溶解，将红棕色粘稠状反应物倒入冰块上，析出大量柠檬黄固体，过滤用苯重结晶得纯品3,5-二硝基-2-羟基苯甲醛7.7克. 产率86%

实施例5：乙烯基芳胺的制备

氩气氛下51mmol甲基三苯基溴化鏻溶解于50ml干燥的四氢呋喃中，冰水冷却，依次加入32ml 1.6M的正丁基锂，30分钟后向其中加入100ml溶有50mmol的邻硝基苯甲醛的四氢呋喃溶液，反应12小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯／已烷1:1，得黄色液体一邻硝基苯乙烯6.63g，产率89.0%。将所得邻硝基苯乙烯45mmol溶于50ml冰醋酸和50ml无水乙醇的混合溶液中加

入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时，冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体一邻氨基苯乙烯 3.2g，产率 60.0%。

实施例 6：乙烯基芳胺的制备

操作同实施例 5，其中间硝基苯甲醛的用量为 50mmol，制得间氨基苯乙烯 2.17g，产率 41.5%。

实施例 7：乙烯基芳胺的制备

操作同实施例 5，其中对硝基苯甲醛的用量为 50mmol，制得对氨基苯乙烯 3.02g，产率 50.7%。

实施例 8：乙烯基芳胺的制备

氩气氛下 74mmol 甲基三苯基溴化鏻溶解于 70ml 干燥的四氢呋喃中，冰水冷却，依次加入 48.8ml 1.6M 的正丁基锂，50 分钟后向其中加入 100ml 溶有 74mmol 的 3-硝基 4-甲基苯甲醛的四氢呋喃溶液，搅拌反应 16 小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯／已烷 1:1，得黄色液体一3-硝基 4-甲基苯乙烯 8.68g，产率 72.0%。将所得邻硝基苯乙烯 45mmol 溶于 50ml 冰醋酸和 50ml 无水乙醇的混合溶液中加入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时，冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体一3-氨基 4-甲基苯乙烯 3.41g，产率 57%。

实施例 9：乙烯基芳胺的制备

氩气氛下 60mmol 甲基三苯基溴化鏻溶解于 60ml 干燥的四氢呋喃中，冰水冷却，依次加入 37.5ml 1.6M 正丁基锂，60 分钟后向其中加入 100ml 溶有 60mmol 的 3-异丙基 4-硝基苯甲醛的四氢呋喃溶液，搅拌反应 18 小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯／已烷 1:1，得黄色液体—3-异丙基 4-硝基苯乙烯 9.11g，产率 79.5%。将所得邻硝基苯乙烯 45mmol 溶于 50ml 冰醋酸和 50ml 无水乙醇的混合溶液中加入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时,冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体—3-异丙基 4-氨基苯乙烯 4.06g，产率 56.0%。

实施例 10：烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.2 摩尔和烯丙烃基氯 0.1 摩尔加热回流 8 小时，冷却放置过夜，倾入 400 毫升水中，用氢氧化钠溶液碱化，乙醚萃取，真空减压蒸馏得 N-烯丙烃基-2,6-二异丙基苯胺 18.33 克. 产率为 84%。以 100 毫升甲苯为溶剂加入 N-烯丙烃基-2,6-二异丙基苯胺 0.084 摩尔和无水氯化锌 0.1 摩尔，氩气气氛下回流 5 小时，冷却后倾入氢氧化钠水溶液中碱化，分离出有机层，下层不溶物溶于热的浓盐酸中，再倾入上述乙醚萃取液中，无水硫酸镁干燥，真空浓缩后减压蒸馏得 4-烯丙烃基-2,6-二异丙基苯胺 12.92 克. 产率为 71%.

实施例 11：烯丙基类芳胺的制备

将 2-特丁基苯胺 0.1 摩尔和 1-溴-2-丁烯烃基 0.05 摩尔加热回

流 10 小时，冷却放置过夜，倾入 200 毫升水中，用氢氧化钠溶液碱化，乙醚萃取，真空减压蒸馏得 N-(2-甲基丙烯基)-2-特丁基苯胺 5.35 克. 产率 53%。以 200 毫升甲苯为溶剂加入 N-(2-甲基丙烯基)-2-特丁基苯胺 0.2 摩尔和无水氯化锌 0.2 摩尔，氩气气氛下回流 8 小时，冷却后倾入氢氧化钠水溶液中碱化，分离出有机层，下层不溶物溶于热的浓盐酸中，再倾入上述乙醚萃取液中，无水硫酸镁干燥，真空浓缩后减压蒸馏得 4-(2-甲基丙烯基)-2-特丁基苯胺 24.89 克. 产率 61%.

实施例 12：烯丙基类芳胺的制备

将 2,6-二甲基苯胺 0.12 摩尔和 1-溴-2-戊烯 0.06 摩尔加热回流 9 小时，冷却放置过夜，倾入 300 毫升水中，用氢氧化钠溶液碱化，乙醚萃取，真空减压蒸馏得 N-(2-乙基丙烯基)-2,6-二甲基苯胺 3.72 克. 产率为 33%。以 80 毫升甲苯为溶剂加入 N-(2-乙基丙烯基)-2,6-二甲基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔，氩气气氛下回流 7 小时，冷却后倾入氢氧化钠水溶液中碱化，分离出有机层，下层不溶物溶于热的浓盐酸中，再倾入上述乙醚萃取液中，无水硫酸镁干燥，真空浓缩后减压蒸馏得 4-烯丙烃基-2,6-二异丙基苯胺 2.77 克. 产率为 29%.

实施例 13：烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.1 摩尔和 1-溴-2-庚烯 0.05 摩尔加热回流 10 小时，冷却放置过夜，倾入 300 毫升水中，用氢氧化钠溶液碱化，乙醚萃取，真空减压蒸馏得 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 4.09 克. 产率为 30%。以 50 毫升甲苯为溶剂加入 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔，氩气气氛下回流 8 小时，冷却后倾入氢氧化钠水溶液中碱化，分离出有机层，下层不溶物溶于热的浓盐酸中，再倾入上述乙醚萃取液中，无水硫酸镁

干燥，真空浓缩后减压蒸馏得 4-(2-丁基烯丙烃基)-2,6-二异丙基苯胺 3.44 克. 产率为 25%.

实施例 14:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

在氮气气氛下，以 10 毫升乙醇为溶剂，2 滴甲酸为催化剂，20 毫摩尔邻羟基苯甲醛与 21 毫摩尔 2-乙烯基苯胺室温下反应 36 小时，反应混合物冷却，过滤，用冷的乙醇洗涤，真空干燥得黄色邻羟基芳亚胺类双齿配体 $C_{15}H_{13}NO$ 3.1 克。产率为 70%。

实施例 15:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

在氮气气氛下，以 15 毫升甲醇为溶剂，2 滴甲酸为催化剂，20 毫摩尔 5-甲基-3-特丁基-2-羟基苯甲醛与 21 毫摩尔 3-胺基-4-甲基苯乙烯室温下反应 36 小时，反应混合物冷却，过滤，用冷的甲醇洗涤，真空干燥得黄色邻羟基芳亚胺类双齿配体 $C_{20}H_{25}NO$ 4.4 克。产率为 75%。

实施例 16:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

在氮气气氛下，以 10 毫升甲醇为溶剂，3 滴甲酸为催化剂，20 毫摩尔 3，5-二硝基-2-羟基苯甲醛与 21 毫摩尔 4-烯丙基-2，6-二异丙基苯胺室温下反应 40 小时，反应混合物冷却，过滤，用冷的甲醇洗涤，真空干燥得黄色邻羟基芳亚胺类双齿配体 $C_{22}H_{25}N_3O_5$ 5.8 克. 产率为 70%.

实施例 17:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

在氮气气氛下，以 20 毫升乙醇为溶剂，0.2 毫升甲酸为催化剂，20 毫摩尔 3-苯基-2-羟基苯甲醛与 21 毫摩尔 4-烯丙烃基-2，6-二甲基苯胺回流反应 8 小时，反应混合物冷却，过滤，用冷的乙醇洗涤，真空干燥得黄色邻羟基芳亚胺类双齿配体 $C_{24}H_{23}NO$ 5.7 克. 产率为 83%.

实施例 18:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

操作同实施例 17，20 毫摩尔 3-苯基-2-羟基苯甲醛与 21 毫摩尔 4-烯丙烃基-2，6-二异丙基基苯胺回流反应 8 小时，得黄色邻羟基芳亚胺类双齿配体 $C_{26}H_{27}NO$ 6.5 克，产率 82%。

实施例 19:含有烯烃基团的邻羟基芳亚胺类双齿配体的制备

在氮气气氛下,以 20 毫升甲醇为溶剂,0.2 毫升甲酸为催化剂,2.0 毫摩尔 3-（9-蒽基）-2-羟基苯甲醛与 2.1 毫摩尔 4-（2-乙基）烯丙烃基-2，6-二异丙基苯胺室温下反应 20 小时,反应混合物冷却,过滤,用冷的甲醇或乙醇洗涤,真空干燥得黄色邻羟基芳亚胺类双齿配体 $C_{35}H_{35}NO$ 8.7 克.产率为 89%。

实施例 20：催化剂 A 组分的制备

在无水无氧条件下，1.5 毫摩尔实施例 14 得到的邻羟基芳亚胺类氮氧双齿配体 $C_{15}H_{13}NO$ 溶解于 50 毫升四氢呋喃，加到 5.0 毫摩尔氢化钠中反应 4 小时后，过滤，真空除去溶剂得配体钠盐。再将钠盐溶于 30 毫升苯溶剂中，慢慢滴加到溶有 1.44 毫摩尔 trans-[Ni(Ph)Cl(PPh$_3$)$_2$]的 50ml 苯溶液中，反应 12 小时后过滤，真空浓缩除去溶剂，干燥得粉末状催化剂固体 $C_{45}H_{43}NOPNi$ 0.78 克,产率 74%。

实施例 21：催化剂 A 组分的制备

在无水无氧条件下，1.5 毫摩尔实施例 18 得到的邻羟基芳亚胺类氮氧双齿配体 $C_{26}H_{27}NO$ 溶解于 50 毫升四氢呋喃，加到 5.0 毫摩尔氢化钠中反应 8 小时后，过滤，真空除去溶剂得配体钠盐。再将钠盐溶于 40ml 苯溶剂中,慢慢滴加到溶有 1.44 毫摩尔 trans-[Ni(Ph)Cl(PPh$_3$)$_2$]的 50ml 苯溶液中，反应 12 小时后过滤，真空浓缩除去溶剂，干燥得粉末状催化剂固体 $C_{52}H_{49}NOPNi$ 0.84 克,产率 71%。

实施例 22：催化剂 A 组分的制备

在无水无氧条件下，1.5 毫摩尔实施例 16 得到的邻羟基芳亚胺类氮氧双齿配体 $C_{22}H_{25}N_3O_5$ 溶解于 50 毫升四氢呋喃，加到 5.0 毫摩尔氢化钠中反应 6 小时后，过滤，真空除去溶剂得配体钠盐。再将钠盐溶于 50ml 苯溶剂中，慢慢滴加到溶有 1.44 毫摩尔 trans-[Ni(Ph)Cl(PPh_3)$_2$ 的 50ml 苯溶液中，反应 12 小时后过滤，真空浓缩除去溶剂，干燥得粉末状催化剂固体 $C_{45}H_{41}N_3O_5PNi$ 0.88 克。产率 77%。

实施例 23：催化剂 A 组分的制备

在无水无氧条件下，1.5 毫摩尔实施例 19 得到的邻羟基芳亚胺类氮氧双齿配体 $C_{35}H_{35}NO$ 溶解于 50 毫升四氢呋喃，加到 5.0 毫摩尔氢化钠中反应 6 小时后，过滤，真空除去溶剂得配体钠盐。再将钠盐溶于 50ml 苯溶剂中，慢慢滴加到溶有 1.44 毫摩尔 trans-[Ni(Ph)Cl(PPh_3)$_2$ 的 50ml 苯溶液中，反应 12 小时后过滤，真空浓缩除去溶剂，干燥得粉末状催化剂固体 $C_{65}H_{59}NOPNi$ 0.94 克. 产率 65%。

实施例 24：乙烯聚合

无氧无水条件下，在 500ml 玻璃反应瓶中加人 120ml 甲苯，实施例 21 得到的催化剂 $C_{52}H_{49}NOPNi$ 65μmol，换气三次后，保持在室温和 4atm 的乙烯压力下聚合 1 小时。用含 10% 盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤 3 次，并于 40℃真空干燥 24 小时，得聚合物 10.9 克，催化效率为 2.0×10^5 g PE/(mol・Ni・hr)。

实施例 25 乙烯聚合

操作同实施例 24，在 2atm 的乙烯压力下聚合 2 小时，得聚合

物12.2克，催化效率为0.9×10^5 g PE/(mol·Ni·hr)。

实施例26：乙烯聚合

在无氧无水条件下，在500ml玻璃反应瓶中加入120ml甲苯，实施例20得到的催化剂$C_{45}H_{43}NOPNi$ 65μmol和助催化剂$Ni(COD)_2$130μmol，换气三次后，保持在室温和7atm的乙烯压力下聚合50分钟。用含10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤3次，并于40℃真空干燥24小时，得聚合物14.6克，催化效率为2.1×10^5 g PE/(mol·Ni·hr)。

实施例27：乙烯聚合

在无氧无水条件下，在500ml玻璃反应瓶中加入120ml甲苯，实施例21得到的催化剂$C_{52}H_{49}NOPNi$ 33μmol，换气三次后，保持在室温和3atm的乙烯压力下聚合1.5小时。用含10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤3次，并于40℃真空干燥24小时，得聚合物2.1克，催化效率为0.45×10^5 g PE/(mol·Ni·hr)。

实施例28：乙烯聚合

在无氧无水条件下，在500ml玻璃反应瓶中加入120ml正己烷，实施例21得到的催化剂$C_{52}H_{49}NOPNi$ 10μmol，换气三次后，保持在室温和7atm的乙烯压力下聚合1小时。用含10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤3次，并于40℃真空干燥24小时，得聚合物2.3克，催化效率为1.1×10^6 g PE/(mol·Ni·hr)。

实施例29：乙烯聚合

在无氧无水条件下，在500ml玻璃反应瓶中加入120ml甲苯，

实施例20得到的催化剂$C_{45}H_{43}NOPNi$ 65μmol和助催化剂五氟苯硼[$B(C_6F_5)_3$] 130μmol，换气三次后，保持在室温和7atm的乙烯压力下聚合50分钟。用含10%盐酸的甲醇溶液终止反应，将所得聚合物过滤，甲醇洗涤3次，并于40℃真空干燥24小时，得聚合物14.6克，催化效率为2.0×10^5 g PE/(mol・Ni・hr)。